CLAIMS

1. Process for manufacturing a part with a determined shape designed to form all or part of an anode for the production of aluminium by fused bath electrolysis and containing a cermet comprising at least one metallic oxide with spinel structure and at least one metallic phase, comprising:

- preparation of a powder containing at least one mixed oxide with spinel structure in which one of the constituents is a metal R present in the form of cations, the said metal R being wholly or partly reducible by a reduction operation, so as to form all or part of the said metallic phase, the said reduction operation being carried out at least partly during the manufacturing process of the said part,
- preparation of a mixture containing the said powder and a binder,
- shaping of the said part by compaction of the mix,
- a debinding operation of the said part,
- a sintering operation of the said part.

2. Manufacturing process according to claim 1, in which the metal R is at least one metal chosen from among copper, nickel, iron and cobalt.

3. Manufacturing process according to claim 1 or 2, in which the said mixed oxide contains at least one metal M, that can exist in at least two valence states M^{n+} and $M^{(n-1)+}$, as a constituent in the form of cations.

4. Manufacturing process according to claim 3, in which the said metal M is chosen from among iron, molybdenum, manganese, vanadium, cobalt and chromium.

5. Manufacturing process according to any one of claims 1 to 4, in which the said mixed oxide also contains as a constituent at least one metal in which the cation reduces the solubility of the mixed oxide with spinel structure in molten cryolite.

6. Manufacturing process according to claim 5, in which the said metal is chosen from among nickel, chromium and tin.

7. Manufacturing process according to any one of claims 1 to 6, in which the said mixed oxide contains at least one metal with a valence state of more than 3.

8. Manufacturing process according to claim 7, in which the said metal is chosen particularly from among titanium, zirconium, hafnium, vanadium, molybdenum and tungsten.

9. Manufacturing process according to any one of claims 1 to 8, in which the said mixed oxide is obtained by a "spray - pyrolysis" process comprising:

- preparation of at least one salt of the metallic elements that will form the mixed oxide;
- dissolution of the said salt(s), or putting them into suspension, in a carrier fluid;
- spraying of the said solution and / or the said suspension at a sufficiently high temperature to cause evaporation of the carrier fluid and thermal

decomposition of the said salt(s), so as to obtain the said mixed oxide.

10. Manufacturing process according to claim 9, in which the said salt is prepared by a mineral acid attack on pure metals.

11. Manufacturing process according to any one of claims 1 to 10, also comprising an "atomisation" operation on the mixture before the shaping step comprising:

- putting the mixture into suspension in a carrier fluid,
- spraying of the suspension so as to completely dry the suspension before its collection and handling.

12. Manufacturing process according to any one of claims 1 to 11, in which the said reduction is controlled.

13. Manufacturing process according to any one of claims 1 to 12, in which the said reduction operation is wholly or partly done on the part after the debinding operation.

14. Manufacturing process according to claim 13, in which the debinding operation of the part includes a heat treatment under an oxidising atmosphere that can decompose the binder in the form of CO_2 and water vapour, and the reduction operation is carried out under a reducing atmosphere that subjects the debinded part to the action of a reducing agent that reduces all or some of the cations of the metal R present in the said mixed oxide, to the metallic state.

15. Manufacturing process according to claim 14, in which the reducing agent is chosen from among hydrogen, carbon monoxide, ammonia and mixtures of them.

16. Manufacturing process according to claim 14 or 15, in which the said reducing atmosphere is a mixture of inert gas and the said reducing agent.

17. Manufacturing process according to claim 14 or 15, in which the said reducing atmosphere is a mixture of inert gas and hydrogen containing 0.5 to 10% of hydrogen by volume.

18. Manufacturing process according to any one of claims 1 to 12, in which the said reduction operation is done wholly or partly on the part during the debinding operation.

19. Manufacturing process according to claim 18, in which the debinding operation of the part includes a debinding and reduction heat treatment under a controlled atmosphere in which the reducing agent is the binder or decomposition products of the binder.

20. Manufacturing process according to any one of claims 1 to 12, in which the said reduction operation is carried out wholly or partly on the powder containing the mixed oxide, before the binder is introduced.

21. Manufacturing process according to claim 20, in which the debinding operation is done under a controlled atmosphere, so as to avoid reoxidation of the metal.

22. Manufacturing process according to either claim 20 or 21, in which the powder containing the mixed oxide also contains a determined proportion of a powder of a

carbonaceous material intended to reduce wholly or partly the said metal R during the reduction operation.

23. Manufacturing process according to claim 22, in which the carbonaceous material is chosen from among carbon black and graphite.

24. Manufacturing process according to any one of claims 20 to 23, in which the powder containing the mixed oxide also contains a determined proportion of a powder of an organometallic compound containing at least the said metal R in the form of a cation, intended to wholly or partly reduce the said metal R during the reduction operation.

25. Manufacturing process according to claim 24, in which the organometallic compound is chosen from among oxalates.

26. Manufacturing process according to any one of claims 1 to 25, in which the said mixture also contains a determined proportion of a powder of a carbonaceous material intended to wholly or partly reduce the said metal R during the reduction operation.

27. Manufacturing process according to claim 26, in which the carbonaceous material is chosen from among carbon black and graphite.

28. Manufacturing process according to any one of claims 1 to 27, in which the said mixture also contains a determined proportion of a powder of an organometallic compound containing at least the said metal R in the form of a cation, intended to wholly or partly reduce the said metal R during the reduction operation.

29. Manufacturing process according to claim 28, in which the organometallic compound is chosen from among oxalates.

30. Manufacturing process according to any one of claims 1 to 29, in which the said reduction operation is carried out so as to enable reduction of a predetermined proportion of cations of the metal R, to the metallic state.

31. Manufacturing process according to claim 30, in which the reduction operation is done at a temperature between 200 and 750°C.

32. Manufacturing process according to claim 30, in which the reduction operation is done at a temperature between 250 and 550°C.

33. Manufacturing process according to claim 30, in which the reduction operation is done at a temperature between 300 and 450°C.

34. Manufacturing process according to any one of claims 30 to 33, in which the reduction operation is done for a time that can vary from 0.5 to 10 h.

35. Manufacturing process according to any one of claims 1 to 34, in which the said reduction operation is done so as to obtain a proportion of metallic phase in the cermet equal to between 10 and 30% by weight.

36. Manufacturing process according to any one of claims 1 to 35, in which the said mixed oxide with spinel structure has a chemical composition which, apart from any doping agent(s) that may be present, satisfies the generic formula (I):

$$X_xR_yZ_zM_{3-x-y-z}\,O^{2-}{}_{4+\delta} \qquad (I)$$

in which:

R represents at least one metal chosen from among copper, nickel, iron and cobalt in the form of cations,

X represents at least one metal chosen from among nickel, chromium, aluminium and tin, in the form of cations,

Z represents a metal chosen from among titanium, zirconium, hafnium, vanadium, molybdenum and tungsten, in the form of cations,

M represents at least one metal that may have two valence states, differing by one valence unit, chosen from among iron, molybdenum, manganese, vanadium, cobalt and copper, in the form of cations,

x, y, z and $(4+\delta)$ are numbers representing quantities of X, R, Z and O^{2-} ions respectively,

x may vary from 0.1 to 2.0,

y may vary from 0.05 to 1.0,

z is less than 1,

the sum (x+y+z) is less than 3,

δ is a positive, negative or zero number, such that the spinel oxide with formula I is electrically neutral.

37. Manufacturing process according to claim 36, in which the chemical composition according to formula I has at least one of the following characteristics:

- x is a number that can vary from 0.3 to 0.7,
- y is a number that can vary from 0.3 to 0.7,

- z is a number that can vary from 0.1 to 0.3.

38. Manufacturing process according to any one of claims 1 to 37, in which the said mixture also contains at least one doping agent.

39. Manufacturing process according to claim 38, in which the doping agent is present in the form of oxides, chemical elements or metals.

40. Manufacturing process according to claim 38 or 39, in which the doping agent is present in a proportion by weight that does not exceed 5% by weight.

41. Manufacturing process according to any one of claims 1 to 40, in which the said mixture also contains another metallic oxide capable of forming a biphase oxides system with the said mixed oxide.

42. Manufacturing process according to any one of claims 1 to 41, in which the said mixture also contains at least one metal that is difficult to oxidise at a temperature below 1000°C.

43. Manufacturing process according to claim 42, in which the said metal that is difficult to oxidise is chosen from among Ag, Au, Pd, Pt or mixtures or alloys of them.

44. Use of an anode comprising at least one part obtained using the process according to any one of claims 1 to 43 for the production of aluminium by fused bath electrolysis.

45. Electrolytic cell comprising at least an anode comprising at least one part obtained using the process according to any one of claims 1 to 43.

46. Sintered cermet part with a determined shape enabling its use as an anode for the production of aluminium, in which the chemical composition of the ceramic phase of the cermet, apart from the doping agents that may be present, satisfies formula II:

$$X_{x'}R_{y'}Z_{z}M'_{3-x'-y'-z}\,O^{2-}_{4+\delta} \qquad \text{(I)}$$

in which:

R represents at least one metal chosen from among copper, nickel, iron and cobalt, in the form of cations,

X represents at least one metal chosen from among nickel, chromium, aluminium and tin, in the form of cations,

Z represents at least one metal chosen from among titanium, zirconium, hafnium, vanadium, molybdenum and tungsten, in the form of cations,

M' represents cations of the same metal that may have two different valence states, differing by one valence unit, n and n-1, the said cations being present in the product with formula II, partly in the form of M'^{n+} cations and partly in the form of $M'^{(n-1)+}$ cations, the number of $M'^{n+}/M'^{(n-1)+}$ pairs being sufficient to assure that the cermet has an electrical conductivity at least equal to a predetermined value, where M' is at least one metal chosen particularly from among iron, molybdenum, manganese, vanadium, cobalt and copper,

x', y', z and (4+δ) represent the quantities of X, R, Z, M' and O^{2-} ions respectively,

x' may vary from 0.1 to 2.0,

y' is equal to zero or a number less than 0.05,

z is less than 1.5,

the sum $(x'+y'+z)$ is less than 3,

δ is a positive, negative or zero number, such that the spinel oxide with formula II is electrically neutral,

and in which the metallic phase is in the form of individual particles distributed in the spinel matrix.